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Optically Detected Magnetic Resonance Study of Core-Shell and Alloy Nanocrystals of HgTe and CdS

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ABSTRACT

The synthesis of HgTe nanocrystals (NCs), coated with a CdS shell, presumably results in the formation of HgTe/CdS, HgTe/CdHgS core-shell structures or separated CdHgS alloys. Photoluminescence (PL), continuous-wave (cw) and time-resolved optically detected magnetic resonance (ODMR) spectroscopy examined the magneto-optical properties of the dominating resonance aforementioned products. The cw ODMR measurements indicated that the NCs exhibit a band, centered at 0.39 Tesla, corresponding to an excited state electron (e) and hole (h) spin manifold, with total angular momentum (F=S+L) $F_e=1/2$ and $F_h=3/2$, respectively. Theoretical simulation of the ODMR band revealed an anisotropy of the g-factor, indicating the existence of trapped carriers' at a mixed Cd-Hg tetrahedral site, confirming the formation of an alloy component. The time-resolved ODMR measurements reveal a characteristic radiative decay time and spin-lattice relaxation time of these trapped carriers of hundreds of microseconds.

INTRODUCTION

The chemical synthesis of colloidal HgTe NCs in aqueous solution was recently reported [1,2]. This novel material exhibits an emission band in the near infrared spectral regime, with giant intensity and a tunable energy, varying with the NCs' size. Therefore, these NCs are currently of great technological interest as emitting materials for thin-film electroluminescence devices, and as optical amplifier media for telecommunication networks. These recent studies [2] indicated that the bare HgTe NCs show "aging" processes and temperature instability, associated with the surface reactivity, which deteriorates the luminescence quantum efficiency. Therefore, the authors of ref. [1] and [2] suggested to improve the surface quality by capping the HgTe NCs with epitaxial layers of another semiconductor (e.g., CdS, CdHgS), to form a core-shell structure [3]. The current work shows our attempts to chemically identify carriers' trapping sites either at the core, the shell or at interface defects, by the use of photoluminescence (PL), continuous-wave and time-resolved optically detected magnetic resonance (ODMR) spectroscopy.

EXPERIMENTAL

The "bare" thioglycerol stabilized HgTe colloidal NCs were prepared in aqueous solution, at room temperature, using the method described previously [1]. The starting solution contained a 4:1 ratio of the Hg^{2+} and Te^{2-} ions. The core-shell structures were prepared by the addition of Cd-perchlorate and addition of H_2S to form a shell of CdS (> 2 nm thick) according to the synthetic conditions mentioned in reference [3]. However, the existence of excess Hg^{2+} ions in the original solution may lead to the formation of a CdHgS alloy as the coating over the "bare" NCs. This assumption will be clarified by the following

spectroscopic measurements. It should be indicated that the radius of the HgTe core was on the order of the shell thickness.

The PL and ODMR spectra were recorded at liquid helium temperature, by immersing the samples in a capillary-type Janis cryogenic Dewar. The PL spectra were obtained by exciting the sample with a 2.70 eV Ar^+ laser. The emitted light was selected by a holographic grating monochromator, and detected with a Hamamatsu Si –photodiode.

The ODMR spectra were obtained by measuring the difference in luminescence intensity (using a Si photodiode), ΔI_{PL}, induced by a magnetic resonance event at the excited state. The ODMR spectra were recorded by mounting the sample on a special probe consisting of a resonance cavity (TE_{111}, with Q-factor of 1000), coupled to a variable frequency microwave (MW) source (v_{MW}=10.76 GHz), surrounded by a split Helmholtz coil superconducting magnet, B_0. The apertures in the cavity and in the superconducting magnet enable optical excess both in the Faraday ($B_0\|$emission) and Voight ($B_0\perp$emission) configurations.

RESULTS

A representative PL spectrum of the HgTe/CdHgS sample is shown in Fig. 1. It consists of a dominating band centered at 668 nm and additional shoulders at 820 nm, 1050 nm and 1240 nm. Most of the PL spectrum overlaps with the absorption spectrum of the size-quantized HgTe NCs which exhibit a bandedge absorption at about 1000 nm.

Magnetic resonance effects were observed in the spectral regime between 550 - 1000 nm. The corresponding non-polarized ODMR spectra, recorded in both Faraday and Voight configurations, showed only a difference in their relative intensities (see Fig. 2a). The circular polarized ODMR spectra, recorded in the Faraday configuration with σ+ and σ- detection, are shown in Fig. 2b. The circular components have a similar band shape and intensity, however they are shifted one with respect to the other by 0.0055 Tesla.

The cw ODMR spectra of the studied sample, recorded with various μW modulation frequencies, are shown in Fig. 3a. It can be seen, that upon an increase in the modulation frequency, the ODMR band intensity is quenched and becomes slightly asymmetric. Furthermore, at a frequency of 819 Hz the high magnetic field component reverses its sign to
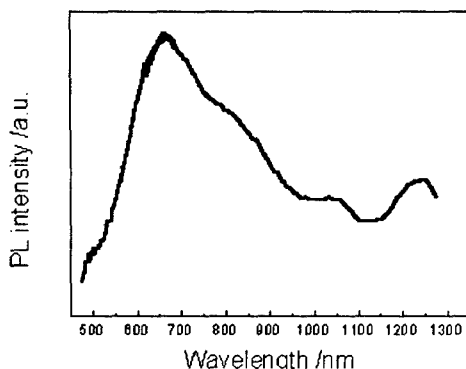

Figure 1. The photoluminescence spectrum of HgTe/CdHgS nanocrystals.

a negative signal. This suggests that the ODMR spectra actually consist of two bands, associated with two separate events with different relaxation times. A representative simulation of the ODMR spectrum with 217 Hz modulation is shown in Fig. 3b. This spectrum consists of a positive Gaussian narrow band centered at 0.395 Tesla (labeled I), overlapping a wide band, centered at 0.379 Tesla (labeled II).

A time-resolved ODMR spectrum is shown by the solid line in Fig. 4, while the MW on/off period of 967 microseconds is presented by the dashed line below. It can be seen from the figure that the PL intensity increases at the rising edge of the MW pulse, change gradually through the pulse, followed by a drastic decay at the end of the pulse.

The spin and radiative relaxation processes, leading to the transient picture and the simulated line (labeled by triangles) shown in Fig. 4, will be discussed in the next section.

DISCUSSION

The PL spectrum of the studied sample showed dominated band at 668 nm and additional shoulders at lower energies. The 1250 nm shoulder in particular resemble the typical luminescence of "bare" size-quantized HgTe NCs or a core component of a core-shell structure [3]. However, the 668 nm and the other shoulders at 820 nm and 1050 nm may correspond to the luminescence of the following species: (a) surface states in pure CdS NCs [4], (b) separate CdHgS NCs' alloys [5], or (c) emission from the shell component of HgTe/CdHgS core-shell
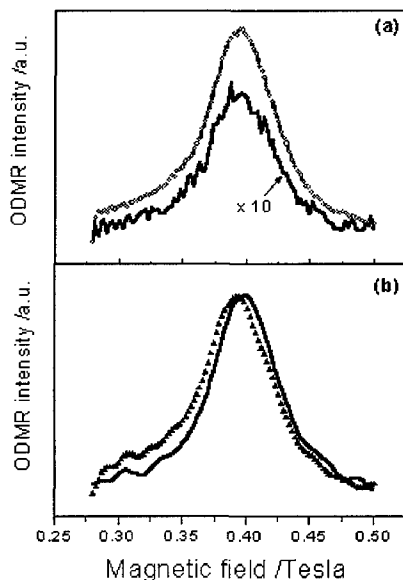

Figure 2. ODMR spectra recorded at Faraday (solid line) and Voight (open dots) configurations (a); σ^+ (solid line) and σ^- (dashed line) polarized detection of the ODMR signal at Faraday configuration

structure. The preparation of the core-shell structure involves an addition of Cd- and S-ions raising a competition between coating of the existing HgTe surfaces and a nucleation of separate CdS NCs. As indicated above, the existence of excess Hg-ions in the initial solution may lead to the formation of either separated CdHgS NCs alloys or HgTe/CdHgS core-shell NCs. The present ODMR measurements enable us to exclude the existence of pure CdS NCs, their typical magnetic resonance spectrum exhibit a different paramagnetic behavior [4]. Thus, the resonance bands shown in Fig. 2 and 3 should correspond to the CdHgS components.

The observed ODMR spectra are associated with a spin flip in the excited state of an electron and a hole. It is assumed that the electron and hole have unpaired spins of $S_e = 1/2$ and $S_h = 1/2$, an angular momentum of $L_e=0$ and $L_h=0, 1$ and a spin-orbit of $F=S+L$. The projections of F in the direction of an external magnetic field (B∥z) have the values of $m_e = \pm1/2$ and $m_h = \pm3/2, \pm1/2$. These projections split in the presence of an external magnetic field by a Zeeman interaction, $\beta g^{iso}B$ (β and g^{iso} are the Bohr magneton and isotropic g spectroscopic factor, respectively). The observation of circularly polarized ODMR signals reveals that the emitting spin state has a total spin (F_e+F_h) of ±1, suggesting the involvement of annihilation between an electron with $m_e=\pm1/2$ and a hole with $m_h=\pm3/2$, as shown in the diagram of Fig. 3c. The solid arrows in the figure correspond to the magnetic resonance transitions (consisting of a flip of the electron spins), while the dashed lines represent the optical transitions. The anticipated spectra are shown below the diagram, while the shift
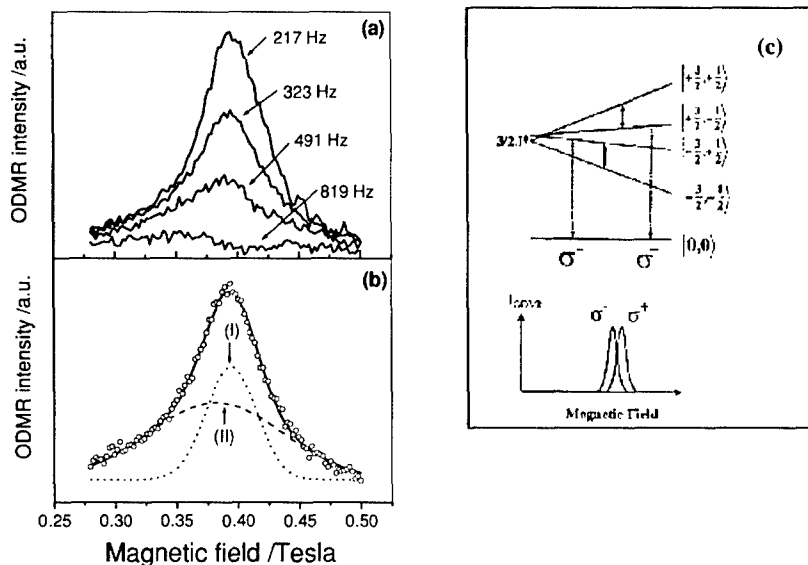

Figure 3. ODMR spectra recorded in Faraday configuration: (a) as a function of MW modulation frequencies; (b) Gaussian simulation of the ODMR signal, recorded with 217Hz MW modulation (doted and dashed lines are representing the narrow (I) and wide (II) simulation parts, and a solid line is a total simulation (I)+(II); (c) schematic diagram of spin states and corresponding anticipated ODMR spectrum

between the σ^+ and σ^- component is $3J/\beta g_e$, when J is an isotropic electron-hole exchange interaction. Although spin states comprised of $m_e = \pm 1/2$ and $m_h = \pm 1/2$ may be populated, the theory discussed extensively in references [4, 7] predicts a negative resonance band in the Voight configuration, which is in contradiction to the present experimental results, shown in Fig. 2a.

The present ODMR spectra were simulated with a phenomenological spin Hamiltonian containing the electron and hole Zeeman interactions as well as isotropic and anisotropic exchange interactions. The experimental results shown in Fig. 3a and the simulated spectra (Fig. 3b) suggested the existence of two overlapping events. Component I (dotted line) was simulated with the spin Hamiltonian leading to $g_{xx} = 1.995$, $g_{yy} = 1.995$, $g_{zz} = 1.845$ and J=0.225 μeV. The particularly broad component II, on the other hand, could not be simulated by a conventional spin Hamiltonian, reflecting knowledge on a contribution of an additional confinement effect of the orbit motion. The latter effect was discussed in length in a separate publication [6] and will not be extended any longer in this document.

The anisotropy in the g factor of the electron suggests its location in an asymmetric trapping site. Stoichiometric defects which can trap an electron include either M^0 (M=Cd, Hg) or X^{2-} (X=S, Te) vacancies with the latter being more common. The formation of a mixed tetrahedron formed by the substitution of a Cd into a Hg site (or vise versa) inserts an anisotropy around a X^{2-} center. Such an anisotropy is pronounced in the g value of a trapped electron. This further supports the existence of alloy components, either as a separated CdHgS or HgTe/CdHgS NCs.

The time-resolved ODMR response, shown in Fig. 4, was simulated by the following kinetic equations [7],

$$\frac{dn_1}{dt} = -\frac{n_1}{\tau_1} + G - \frac{n_1 - (n_1 + n_2)(1-p)}{T_1} - (n_1 - n_2)P_{MW}$$

$$\frac{dn_2}{dt} = -\frac{n_2}{\tau_2} + G - \frac{n_2 - (n_1 + n_2)p}{T_1} - (n_2 - n_1)P_{MW}$$

$$p = \frac{1}{1 + \exp(\Delta E / kT)} \quad , \quad \Delta E = h\nu_{MW}$$

which include a rate of the spin manifold formation (G), radiative and nonradiative processes ($\tau^{-1} = \tau_{rad}^{-1} + \tau_{nrad}^{-1}$) and spin-lattice relaxation times (T_1). n_1 and n_2 correspond to $|+3/2, -1/2 >$ and $|+3/2, +1/2 >$, or $|-3/2, -1/2 >$ and $|-3/2, +1/2 >$ pair states, shown in Fig. 3c. The gradual change seen in Fig. 4 during the MW pulse is controlled by the radiative lifetime, while the sudden decay at the end of the pulse corresponds to the spin-lattice relaxation time, bringing the system back into a Bolzmann distribution of the population among the spin states. The simulated response, using the above equations, revealed a radiative decay time of 300 microseconds and a spin-lattice relaxation time of 900 microseconds. It should be noted that the ODMR experiment enables to detect relatively slow radiative processes, while the fast decay processes are not detected in the current experiment.
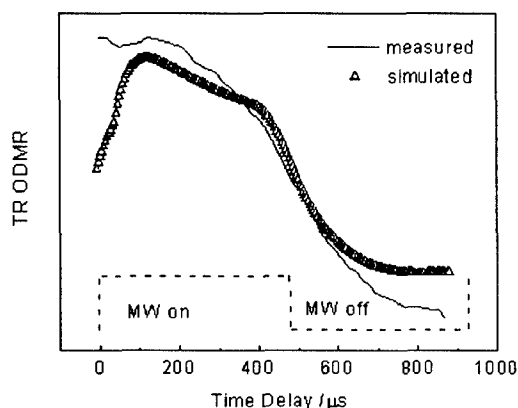
Figure 4. time-resolved ODMR spectra: measured, with the time period of the transient MW pulse (solid line); simulated (triangled line).

CONCLUSIONS

The synthetic approach of coating HgTe nanocrystals with a shell of CdS results in the formation of HgTe/CdS or HgTe/CdHgS core-shell structures or separately formed CdHgS alloys together with the preformed HgTe NCs. The cw ODMR measurements indicated that the NCs exhibit a dominating resonance band corresponding to a recombination between trapped electrons centered at mixed Cd-Hg tetrahedral sites with $F_e=1/2$ and a valence hole with $F_h=3/2$. The suggested anisotropic site indicates the existence of alloy components. The time-resolved ODMR measurements reveal relatively long (hundreds of microseconds) radiative and spin-lattice relaxation times characteristic for the radiative recombination of trapped carriers.

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